

PATENT SPECIFICATION (11)

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(54) A METHOD OF SCAVENGING SULPHIDE

- (71) We, HALLIBURTON COMPANY, a corporation organized under the laws of the State of Delaware, United States of America, of 1015 Bois d'Arc Street, P.O. Drawer 1431, Duncan, Oklahoma 73533, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-
- The present invention is concerned with the scavenging of sulphide from liquids.
- Liquids used in wells penetrating subterranean formations (for example, drilling, completing or servicing liquids used in oil wells or gas wells), liquids produced from and make-up liquids used in such wells, and liquids in sewerage systems frequently contain sulphides, such as hydrogen sulphide.
- Hydrogen sulphide is poisonous and promotes corrosion of steel pipes and tubes which come into contact with liquids containing it. It has therefore been proposed to remove hydrogen sulphide from such liquids either as it is formed or after the liquid has been contaminated by hydrogen sulphide. This process is known as "scavenging".
- It has been proposed in U.S. Patent 3928211 to use zinc hydroxide, zinc carbonate or basic zinc carbonate as the scavenging agent. We have found that these compounds tends to form an insoluble precipitate in which the zinc is unavailable for reaction with hydrogen sulphide, and tend to adversely affect the rheological properties of some liquids, particularly where the liquid contains a clay. Typical adverse effects on the rheological properties include undesired thickening or gelling of the liquid and increased liquid loss.
- We have now developed an improved class of scavenging agents for this purpose. According to the invention, there is provided a method of scavenging sulphide from a liquid having a pH of 5 to 12, in which there is used as the scavenging agent a complex formed between at least one zinc compound and an organic chelating agent, the complex having a stability constant of 10 to 16.
- The scavenging agents used in the method according to the invention have little or no adverse effect on the rheology of the liquid, for example, they do not cause flocculation of clays in the liquid, and the stability constant is such that insoluble zinc hydroxide or zinc oxide is not formed to any appreciable extent.
- The complex has a stability constant of 10 to 16, as mentioned above. The term "stability constant" is defined in "Organic Sequestering Agents" by S. Chaber and A.E. Martell; John Wiley and Sons, Inc., New York, and in "Stability Constants of Metal-Ion Complexes" by L.G. Sillen and A.E. Martell; Metcalf and Cooper Limited, London (1964).
- The scavenging agent used in the method according to the invention may be added to the liquid as a previously prepared complex (either in liquid concentrate, or dry powder form or pre-mixed with water) or, preferably, the complex may be formed *in situ* by reaction of the zinc compound with the chelating agent in the desired ratio in the liquid to be treated. In the latter case, when the liquid to be treated is oil-based (or a dispersion, such as an emulsion, of an oil), it is sometimes desirable to add the zinc compound in the form of a

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solution or dispersion in oil.

When the complex is formed *in situ*, the chelating agent is preferably present in excess of the amount needed to completely chelate the available zinc, whereby precipitation of any clays in the liquid being treated and adsorption of the zinc compound on solids in the liquid being treated, which take place when an ionic zinc compound is used, are avoided. When the liquid being treated is a drilling fluid of high solids content, the zinc compound and the chelating agent should be added slowly and thoroughly mixed with the fluid before it is circulated in the well.

The zinc compound, which preferably contains no anions capable of causing flocculation of any clays in the liquid, may be, for example, a formate, acetate, chloride, bromide, iodide, chlorate, bromate, nitrate, sulphate, sulphoxylate, hydrosulphite or silicofluoride salt. The salt may be water soluble, for example, zinc sulphate or zinc chloride, although it is possible to use less soluble compounds such as zinc carbonate or basic zinc carbonate, even though these involve longer reaction times. It is therefore preferred that when these less soluble compounds are used, the complex is formed before adding it to the liquid. When a zinc carbonate is used, the carbonate ions may be removed from the complex in order to avoid flocculation of clays encountered in the liquid to be treated.

Particularly when hydrogen sulphide and oxygen are both present in the liquid (such as a drilling fluid), the zinc compound is preferably zinc hydrosulphite, which is preferably added to the liquid in the form of a suspension or slurry in an organic carrier liquid, which carrier liquid should be substantially unreactive with the zinc compound, oxygen, hydrogen sulphide and additives to the liquid (such as conventional well fluid additives). Preferred carrier liquids include aliphatic hydrocarbons, aromatic hydrocarbons, substituted hydrocarbons or mixtures thereof, such as mineral oils, diesel oils and kerosene, which should have a viscosity sufficient to suspend the zinc hydrosulphite (and any other additives). A preferred viscosity is at least five centipoise; it may be necessary to add unreactive thickeners, such as silica or polymers. Other optional additives include emulsifiers, surfactants, dispersing agents and modifiers for the pour point, flammability, volatility and colour.

The abovementioned zinc hydrosulphite preferably has a fine particle size (for easier suspension and faster reaction) and is preferably pure (e.g. at least 80% pure). The zinc hydrosulphite, which may be used together with other zinc compounds and/or hydrosulphites, is preferably present in the carrier liquid in a concentration of from 10 to 90% (more preferably 15 to 75% by weight).

For scavenging sulphides from oil based liquids (that is a liquid containing at least one oil or organic liquid phase such as a normally liquid hydrocarbon) or from oil-external emulsion fluids, a preferred scavenger is basic zinc carbonate. This scavenger can be added directly to the liquid as a finely divided particulate material or suspended in a slurry using an organic carrier liquid as described above. For the treatment of oil-external emulsion liquids, the scavenger can be suspended in an aqueous or an organic carrier liquid. The basic zinc carbonate is preferably suspended in the carrier liquid in concentrations of from 10 to 90% by weight more preferably 15 to 75%. Other additives can be used to modify the properties of the carrier liquid, for example, to modify the viscosity, flammability, volatility of colour, as referred to above.

When using zinc hydrosulphite or basic zinc carbonate, as described above, it is not necessary that the zinc compound be chelated with an organic chelating agent.

The chelating agent is preferably a low molecular weight compound having carboxylic acid and/or amino functional groups, for example, a compound having at least one tertiary amine group and at least two carboxyl groups, or a salt thereof, a polyfunctional amine or a hydroxycarboxylic acid.

The following are examples of such chelating agents, the stability constant of the corresponding complex being in parenthesis: dithiotartaric acid (15.85); triethylene tetramine (12.1); ethylene-bis- α,α' -(2-amino-methyl)-pyridine (11.5); β,β',β'' -triaminotriethylamine (14.65); tetrakis (2-amino-ethyl)-ethylene diamine; α,β -diamino propionic acid (11.5); β -mercaptoethyliminodiacetic acid (15.92); ethylene diamine-N, N'-diacetic acid (11.1); ethylene diamine-N, N'-diacetic acid (11.93); ethylene-bis-N, N'-2 (aminomethyl)-pyridine N-N'-diacetic acid (15.2); N-hydroxy ethylethylene diamine tetraacetic acid (HEDTA) (14.5); ethylene diamine N-N' dipropionic N-N'-diacetic acid (14.5); hydroxy acetic acid; and nitrilotriacetic acid (NTA) (11.0). The preferred chelating agent is the NTA which is especially effective for reacting with or absorbing high ratios of hydrogen sulphide with little or no adverse effect on the drilling fluid rheology. Other chelating agents with structures similar to NTA and a stability constant near that of NTA are also effective under typical drilling conditions. The zinc NTA complex is also preferred because it is effective over a wide pH range and reacts practically instantaneously on addition to a drilling fluid to effectively inactivate hydrogen sulphide to prevent stress

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cracking of metals and liberation of hydrogen sulphide at the surface.

When the complex is formed *in situ*, the organic chelating agent should be combined with the soluble zinc compound in a certain weight ratio depending on its sequestering ability. For NTA and similar chelants the preferred range is about 4:1 to 99:1, more preferably from about 4:1 to 9:1.

In the scavenging agent according to the invention, zinc effectively stops stress cracking of ferrous metals without plating out on the metal and causing galvanic corrosion. Furthermore, zinc does not cause stress cracking through secondary oxygen reactions. Zinc sulphide precipitates out when the liquid contains sulphides. This precipitate does not adversely affect the well fluid rheology and can be readily removed by conventional methods such as centrifuging, filtering or settling in mud pits.

The scavenging agents according to the invention are effective over a wide pH range (from 5 to 12), but they are preferably used in the pH range of about 6 to 11. The scavenging agents can be used alone or in conjunction with conventional well fluid additives, even other sulphide scavenging agents. The scavenging agents of this invention can effectively remove hydrogen sulphide concentrations from only trace amounts like one ppm up to large amounts such as thousands of ppm or more by simply adding the amount of chelate needed to stoichiometrically react with the sulphide.

In a preferred method according to the invention, the complex is added to a drilling fluid which is preferably an aqueous dispersed or nondispersed fluid. The drilling fluid can also be an oil-based or emulsion fluid. The oil can be any normally liquid hydrocarbon such as aliphatic hydrocarbon, an aromatic hydrocarbon or mixtures thereof. The fluid is typically circulated in the well during drilling and other operations so that the concentration of complex should be monitored to maintain a certain concentration, preferably from about several parts per million (ppm) to several percent, depending on the likely amount of hydrogen sulphide present. Normally, a concentration of up to about five pounds per barrel (ppb) of fluid will be sufficient. The fluid should also be monitored to indicate the presence of any hydrogen sulphide or sulphide ions which would indicate that more complex should be added or that the concentration of the complex in the liquid should be increased. As a safeguard where hydrogen sulphide is not likely to be a severe problem, chelate concentrations of about 0.25 to 0.5 ppb (1.258 to 2.516 grams per litre) should be used to scavenge out trace amounts of sulphides that may not be detected by tests on the surface.

In order that the invention may be more fully understood, the following Examples are given by way of illustration only.

EXAMPLES

Thirty three 350 ml. samples of a water-based drilling fluid were formulated using water containing the following additives: 0.9 ppb NaCl, 1.75 ppb CaCO_3 , 16 ppb Wyoming bentonite, 28 ppb Southern bentonite, 4 ppb chrome lignosulphonate dispersant and a fluid loss additive. The pH was adjusted to 9.0 with NaOH. Various sulphide scavenging agents were added in the quantities indicated in the following Table 1. (One ppb is one pound per 42-gallon barrel of total fluid and is equal to one gram per 350 millilitres of fluid or about 3 grams per litre of fluid).

When the fluid contained a zinc-containing scavenging agent, the amount of the latter was such that each fluid contained the same molar concentration of zinc metal.

The effect of some additives on stress cracking was evaluated using prestressed steel bearings in some of the drilling fluids at 150°F with rolling; i.e., ageing or hot rolling the sample for the time indicated in the following Table 1.

The majority of the scavenging agents were synthesized by the following steps:

1. Equimolar quantities of the chelating agent and zinc salt were stirred in a minimum amount of water for 30 minutes.

2. The solution was basified (pH 8-9) with KOH.

3. Absolute ethanol was added to precipitate the chelates, which were filtered and dried.

Zinc NTA complexes were prepared by reacting sodium NTA (NTANa_3) with each of the following: ZnCl_2 and ZnSO_4 . These complexes were tested both as slurries and as oven-dried solids.

Some of the fluids were treated with H_2S , as shown in Table 1. When hydrogen sulphide treatment was used, the H_2S was generated from 0.1 M sodium sulphide (Na_2S) with sulphuric acid and the H_2S was bubbled into the drilling fluid sample in a Waring blender. For each 100 ml of 0.1 M Na_2S used, 970 ppm of H_2S was generated for reaction in the drilling fluid. Hydrogen sulphide was bubbled through the sample until H_2S emission was detected by lead acetate paper indicating saturation of the mud with H_2S .

The stability of complexes of lead, zinc, and copper vary according to the metal, chelating agent, pH, etc. With the zinc metal ion chelated by nitrilotriacetic acid (NTA), the

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compounds had little detrimental effect on the drilling fluid properties. Hydrogen sulphide reacts readily with the Cu, Pb, and Zn chelates of NTA, precipitating the sulphide ion as insoluble CuS, PbS, ZnS. Although these compounds are very effective H₂S scavengers, the following results show that only the ZnNTA also prevented sulphide stress cracking of prestressed steel bearings and has no detrimental effects on the drilling mud. In fact, the bearings placed in mud treated with PbNTA and CuNTA often crack before bearings in untreated mud.

The zinc lignosulphonates containing zinc are effective in preventing stress cracking in bearings. However, foaming is a severe problem and the zinc concentration is very low in this complex.

Inorganic compounds of zinc (sodium zincate) and lead (sodium plumbite) are effective H₂S scavengers. However, these compounds fail to prevent sulphide stress cracking of bearings in treated mud.

Rheology, fluid loss and pH for each sample was measured using a Fann type direct reading viscometer, fluid loss cell or pH meter according to API method 13B. The tests indicated that zinc NTA complexes gave acceptable results in preventing stress cracking of steel bearings; however, preblended and purified ZnNTA gave the best results.

TABLE 1

Identification of Samples

Sample No.	Treatment or Additive
1,3,6,8,10,12	Base Fluid without treatment or additive
2,5,9,11,13	2.86 ppb ZnNTA
4	24 ppb of 15% zinc lignosulphonate solution
5	3.98 ppb zinc ethylene diamine tetraacetic acid salt (ZnEDTA)
7	1.12 ppb basic zinc carbonate (ZnCO ₃)
14,19	2 ppb ZnNTA
15	Base Fluid with H ₂ S treatment, no additive.
16	2 ppb ZnCO ₃
17	Base Fluid without treatment or additive
18	Base Fluid with H ₂ S treatment, no additive
20	2 ppb copper carbonate (CuCO ₃)
21	2 ppb ZnEDTA
22	2 ppb ZnDET (diethylene triamine)
23	2 ppb Zn TETA (Triethylene tetra-amine)

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TABLE 1 (Continued)

	Sample No.	Treatment or Additive	
5			5
10	24	Base Fluid with 1 ppb sulphides or 2,494 ppm sulphides. Ageing by hot rolling at 150°F for 16 hours. This base mud contains 4.5 ppb VC-10 chrome ligno-sulphonate dispersant.	10
15	25	Same as Sample 24 with 2.08 ppb basic Zn carbonate containing 45% zinc.	15
	26	Same as Sample 24 with 8.66 ppb ZnNTA containing 21% zinc.	
20	27	Base fluid without treatment or additive.	20
25	28	Same as Sample 24 with 8.6 ppb ZnSO ₄ and Na ₃ NTA mixture containing 21% zinc.	25
	29	Standard base fluid (as Sample 24 without sulphides).	
30	30	Same as Sample 29 with 5 ppb of a mixture of 35:65 weight ratio of ZnSO ₄ :Na ₃ NTA.	30
35	31	Same as Sample 30 with the ratio of 40:60	35
	32	Same as Sample 30 with the ratio of 45:55	
40	33	Same as Sample 30 with the ratio of 50:50.	40

Various properties of the above Samples are indicated in the following Tables 2 to 11.

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TABLE 2

Effect of additive on rheology and reaction with hydrogen sulfide
Initial rheology and H₂S uptake

Sample No.	Set 1			Set 2			Set 3		
	1	2	3	4	5	6	7	8	9
Apparent Viscosity	19.5	16.5	19.5	47.5	28.5	21.5	21.0		
600 Reading	39	33	39	95	57	43	42		
300 Reading	24	20	26	72	40	28	27		
Plastic Viscosity (PV)	15	13	13	23	17	15	15		
Yield Point (YP)	9	7	13	49	23	13	12		
Gel Strength (10 sec.)	3	3	5	4		
Gel Strength (10 min.)	23	27		
Vol. of 0.1 M Na ₂ S (ml) absorbed	15	217	12	..	52**	14	24		
Final Temp. °F	80	102	86	80	90		
Final pH	8.1	6.5	8.1		

*Foamed

**Gelled

Samples 3, 4 and 5 show that zinc lignosulfonate and zinc ethylene diamine tetraacetic acid salt (ZnEDTA) caused excess foaming and gelation of the drilling fluid.
Samples 6 and 7 show that basic zinc carbonate has a very low reactive capacity for H₂S.

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TABLE 3

Rheology after reaction with H₂S

5		Set 1		5
	Sample No.	1	2	
10	Apparent Viscosity	18.5	17.5	
	600 Reading	37	35	10
	300 Reading	22	21	
	Plastic Viscosity (PV)	15	14	
	Yield Point (YP)	7	7	
15	Gel Strength (10 sec.)	4	4	
	Gel Strength (10 min.)	12	25	15
	API Filtrate (ml/30 min.)	8	8	

20 These tests show that the ZnNTA chelate had a high reactive capacity for H₂S with good rheology and fluid loss.

20

TABLE 4

Initial rheology and fluid loss

25		Set 1		25
	Sample No.	8	9	
30	Apparent Viscosity	18	16.5	30
	600 Reading	36	33	
	300 Reading	23	20	
	Plastic Viscosity (PV)	13	13	
	Yield Point (YP)	10	7	
35	Gel Strength (10 sec.)	3	6	
	Gel Strength (10 min.)	14	38	35
	API Filtrate (ml/30 min.)	7.1	6.4	

TABLE 5

Rheology and fluid loss after hotrolling 16 hours at 150°F.

45		Set 1		45
	Sample No.	8	9	
50	Apparent Viscosity	18.5	19.5	
	600 Reading	37	39	50
	300 Reading	22	22	
	Plastic Viscosity (PV)	15	17	
	Yield Point (YP)	7	5	
	Gel Strength (10 sec.)	3	3	
55	Gel Strength (10 min.)	9	3	55
	API Filtrate (ml/30 min.)	6.6	7.6	

60 These tests show that drilling fluid with ZnNTA has good rheology and fluid loss after aging or hotrolling.

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TABLE 6

Initial rheology

		Set 2		Set 4		
5	Sample No.	10	11	12	13	5
	Apparent Viscosity	22	22.5	18	19	
10	600 Reading	44	45	36	38	10
	300 Reading	37	39	22	25	
	Plastic Viscosity	7	6	14	13	
	Yield Point (YP)	30	33	8	12	
	Gel Strength (10 sec.)	5	17	6	13	
15	Gel Strength (10 min.)	14	82	27	58	15

TABLE 7

Rheology, fluid loss, and H₂S uptake after hotrolling 16 hours at 325°F

		Set 2		
25	Sample No.	10	11	25
	Apparent Viscosity	46.5	38	
	600 Reading	93	76	
	300 Reading	62	59	
30	Plastic Viscosity (PV)	31	17	30
	Yield Point (YP)	31	42	
	Gel Strength (10 sec.)	14	4	
	Gel Strength 10 min.)	244	45	
	API Filtrate (ml/30 min.)	12.7	13.5	
35	Vol. of 0.1 M Na ₂ S (ml) absorbed	19	116	35

These tests show that drilling mud with ZnNTA has good rheology and fluid loss after reacting with H₂S and aging.

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TABLE 8

Rheology and H₂S uptake after aging for 8 days at 78°F

		Set 4		
45	Sample No.	12	13	45
	Apparent Viscosity	19	23.5	
50	600 Reading	38	47	50
	300 Reading	24	29	
	Plastic Viscosity (PV)	14	18	
	Yield Point	10	11	
55	Gel Strength (10 sec.)	4	5	55
	Gel Strength (10 min.)	21	26	
	Vol. of 0.1 M Na ₂ S (ml) absorbed	22	60	

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These tests show that drilling mud with ZnNTA has good rheology after heat aging for extended periods with H₂S reaction.

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TABLE 9

Set 1 - Rolled 16 hours

5	Sample No.	Description of Bearing	5
	14	Medium dark; rough surface. no cracks	
	15	Dark; smooth surface; cracked	
10	16	Dark; smooth surface; cracked	10

Set 2 - Rolled 5 hours with 2 Bearings

	20	Dark color; one cracked	
15	21	Black; no cracks	15
	22	Black; no cracks	
	23	Dark; no cracks	

Set 2 -- Rolled 22 Hours

20			20
	17	Both black and cracked	
	18	Both black and cracked	
	19	Both dark; no cracks	
	20	Copper coated; cracked	
25	21	Both black; one cracked	25
	22	Both black; one cracked	
	23	Both black; one cracked	

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TABLE 10

Sulfide Scavengers

Sample No.	Initial	Aging	Effectiveness	Comparison	Initial	Aging	In Situ	Formation	Aging
	24		Initial	Aging	Initial	Aging	27	Initial	28
Apparent Viscosity									
600 RPM	8	11	12	10	18	15	13	22	15
300 RPM	15	22	21	20	33	30	26	44	29
Plastic Viscosity	8	11	12	12	25	16	18	30	17
Yield Point (#/100 ft. ²)	7	11	9	8	8	14	8	14	12
Initial Gel	1	0	3	4	17	2	10	16	5
10 Min. Gel	1	1	1	1	3	1	8	7	2
pH	4	3	20	4	65	15	31	82	50
H ₂ S Remaining	12.4	11.2	12.3	11.0	12.2	10.8	--	12.0	--
Sulfides Remaining	1800	1680	1800	<1.0	15	--	--	--	--
	--	--	--	--	--	--	--	10	3-4

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TABLE 11

Ratio of Zinc to Chelant

Sample No.	Initial 29	Aging	Initial 30	Aging	Initial 31	Aging	Initial 32	Aging	Initial 33	Aging
Apparent Viscosity	16	12	16	15	20	15	23	16	31	16
600 RPM	32	24	33	30	40	30	47	32	62	33
300 RPM	20	14	21	16	25	17	32	19	49	20
Plastic Viscosity	13	10	12	14	15	13	15	13	13	13
Yield Point (#/100 ft. ²)	7	4	9	2	10	4	17	6	36	17
Initial Gel	4	1	2	1	8	1	13	1	22	2
10 Min. Gel	90	3	109	5	144	10	187	20	239	28
pH	..	8.9	..	8.5	..	8.5	..	8.6	..	8.6

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Table 10. Samples 24 to 26. show that ZnNTA effectively removes H_2S from the drilling fluid quickly and for an extended period of time with good rheology of the fluid. ZnNTA reduces the sulphide ion concentration practically instantaneously as compared to basic $ZnCO_3$.

- 5 Samples 27 and 28 of Table 10 show that ZnNTA can be formed *in situ* and react 5
practically instantaneously to remove sulphide ions, reducing the sulphide ion concentra-
tion to only trace amounts.

- 10 Table 11. Samples 29 to 33. show that high ratios of zinc: NTA produces higher gel 10
strength or higher viscosity and yield point at the high additive concentration of 5 ppb. The
weight ratio of zinc ion to NTA should be such that NTA is in a molecular excess relative to
the zinc ion.

EXAMPLE

(Samples 34-40)

- 15 A base mud was prepared using 350 milliliters (ml) deionized water, 88 gm salt, 10 gm 15
attapulgite clay, 5 gm starch and 0.25 gm sodium hydroxide caustic for each sample. To
three samples, portions of ammonium bisulfite (NH_4HSO_3), as a 60% solution in water,
was added and recorded as pounds per 42 gallons per barrel (ppb) or gm per 350 ml sample.
20 To three other samples portions of zinc hydrosulfite, as a 30% slurry in white oil was added 20
and recorded ppb which is equivalent to gm per 350 ml sample. The pH of several samples
was measured and adjusted using caustic. Fourteen ml of sodium sulfide solution was added
to each sample at a concentration of 187.5 gm $Na_2S \cdot 8H_2O$ per 1000 ml of solution in
deionized water. Fourteen milliliters were equivalent to 1000 ppm H_2S in 350 milliliters of
mud. The resulting pH and H_2S present was measured. The H_2S concentration was
25 measured in API filtrate using a Garrett gas train. After hot rolling the samples in an oven 25
at 150°F for 16 hours with the pH and H_2S concentration were again measured.

Measured properties of the samples are tabulated as Table 12:

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TABLE 12

Sample	34	35	36	37	38	39	40
NH ₄ , HSO ₃ (gm or ppb)	Base Mud	1	2	4	1	2	4
Zn hydrosulfite (gm or ppb)	--	--	--	--	--	--	--
pH (before NaOH)	--	--	6.0	5.6	--	--	--
Caustic (gm or ppb)	--	--	0.25	0.75	--	--	--
pH (after NaOH)	--	--	7.4	7.6	--	--	--
pH (after Na ₂ S)	11.6	10.4	9.6	9.3	11.4	11.1	7.7
H ₂ S (ppm)	960	550	400	250	400	640	100
pH							
H ₂ S (ppm)	11.1	After Hot Rolling	9.7	9.1	11.1	10.9	9.2
	480	10.3	175	25	340	120	trace
		300					

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TABLE 13 (Samples 41-43)						
	Sample 41		Sample 42		Sample 43	
	Initial	After Test	Initial	After Test	Initial	After Test
Scavenger		NH ₄ HSO ₃		Zn Hydrosulfide		Na ₂ SO ₃
Fann viscosity						
600 RPM	26	16	22	18	25	28
300 RPM	16	10	14	11	15	19
Apparent Viscosity (AV)	13	8	11	9	12.5	14
Plastic Viscosity (PV)	10	6	8	7	10	9
Yield Point (YP)	6	4	6	4	5	10
Gel Strength, Initial	3	1	2	1	2	6
Gel Strength, 10 min.	22	1	19	2	22	31
pH	11.6	6.5	11.3	7.5	11.3	10.5
Temp. °C	24	24	24.5	24.5	23	23
O ₂ Conc. (ppm)	7.8	--	8.2	--	8.3	--

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EXAMPLE*Sample 41)*

A polymer type aqueous base mud was prepared using the following recipe based on grams (gm) per a 350 milliliter (ml) sample which is proportional to pounds per 42-gallon barrel (ppb):

5	350 ml	- deionized water	
10	12 gm	- bentonite clay	10
	0.05 gm	- polyvinyl acetate-maleic anhydride copolymer bentonite extender	
15	0.5 gm	- AMOCO Drilaid 425 polyacrylamide polymer	15
	0.25 gm	- NaOH caustic	

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The properties of this mud Sample 41 were measured before aerating using air passed through a Garrett gas train dispersion tube and adding ammonium bisulfite (60% in water) dropwise to the mud. The measured and calculated properties are tabulated in Table 13.

After measuring the initial properties the ammonium solution was added dropwise to Sample 41 at 3 drops per 60 seconds with stirring (one drop = 0.027933 gm of NH_4HSO_3) and the oxygen concentration in ppm was recorded. After twenty minutes, addition of the NH_4HSO_3 solution resumed. Recorded values for drops of solution added, oxygen concentration as measured by a YSI oxygen meter in parts per million (ppm) and time in minutes are as follows:

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TABLE 14

	Time	Drops	O ₂ ppm	Time	Drops	O ₂ ppm	
35	0	0	7.8	19:00	57	0.07	35
	1:00	3	7.5	20:00	60	0.07	
	2:00	6	7.0	21:00*	--	0.70	
	3:00	9	6.4	22:00*	--	0.80	
	4:00	12	5.8	23:00*	--	2.00	40
40	5:00	15	5.0	24:00*	--	1.85	
	6:00	18	3.7	25:00*	--	1.75	
	7:00	21	0.9	26:00	--	1.60	
	8:00	24	0.45	27:00	63	1.40	
	9:00	27	0.33	28:00	66	0.55	
45	10:00	30	0.25	29:00	69	0.43	45
	11:00	33	0.20	30:00	72	0.37	
	12:00	36	0.15	31:00	75	0.32	
	13:00	39	0.10	32:00	78	0.26	
	14:00	42	0.09	33:00	81	0.23	
50	15:00	45	0.07	34:00	84	0.18	50
	16:00	48	0.07	35:00	87	0.15	
	17:00	51	0.07	36:00	90	0.14	
	18:00	54	0.07				

55 *Aerating sample

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EXAMPLE

(Sample 42)

Another portion of the polymer base mud (Sample 42) was tested, aerated and treated with a 30% slurry of zinc hydrosulfite in white oil. The properties of Sample 42 are shown in Table 13. The zinc hydrosulfite was added dropwise at 3 drops per minute (one drop being 0.018484 gm of zinc hydrosulfite). The times in minutes, drops of slurry and oxygen concentration in ppm are tabulated as follows:

TABLE 15

	Time	Drops	O ₂ ppm	Time	Drops	O ₂ ppm
	0	0	8.20	18:00	54	0.11
	1:00	3	8.20	19:00	57	0.10
15	2:00	6	8.07	20:00	60	0.10
	3:00	9	7.80	21:00*	--	2.00
	4:00	12	7.48	22:00*	--	3.85
	5:00	15	7.03	23:00*	--	5.20
	6:00	18	6.45	24:00*	--	4.70
20	7:00	21	5.78	25:00*	--	4.30
	8:00	24	5.00	26:00	--	4.00
	9:00	27	4.20	27:00	--	1.40
	10:00	30	3.35	28:00	--	0.90
	11:00	33	2.55	29:00	--	0.57
25	12:00	36	1.65	30:00	--	0.46
	13:00	39	0.75	31:00	--	0.43
	14:00	42	0.30	32:00	63	0.37
	15:00	45	0.20	33:00	66	0.35
	16:00	48	0.15	34:00	69	0.31
30	17:00	51	0.14	35:00	72	0.38

* Aerating Sample

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EXAMPLE*(Sample 43)*

A third portion of polymer base mud (Sample 43) was tested, aerated and treated with a solution of 20 grams of sodium sulfite anhydrous, Na_2SO_3 , per 100 ml of solution with deionized water. The properties of Sample 43 are in Table 13. The sodium sulfite solution was added at 3 and 5 drops per minutes with stirring as for the previous samples (one drop equals 0.0262415 gm of Na_2SO_3). The time in minutes, drops of solution and oxygen concentration in ppm are tabulated as follows:

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TABLE 16

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	Time	Drops	O ₂ ppm	Time	Drops	O ₂ ppm	
	0	0	8.30	22:00	90	6.00	
15	1:00	3	8.28	23:00	95	5.70	15
	2:00	6	8.28	24:00	100	5.20	
	3:00	9	8.28	25:00	105	4.85	
	4:00	12	8.20	26:00	110	4.50	
	5:00	15	8.10	27:00	115	4.15	
20	6:00	18	8.18	28:00	120	3.80	20
	7:00	21	8.11	29:00	125	3.50	
	8:00	24	8.10	30:00	130	3.15	
	9:00	27	8.05	31:00	135	2.73	
	10:00	30	8.0	32:00	140	2.34	
25	9:00	35	7.98	33:00	145	1.90	25
	12:00	40	7.9	34:00	150	1.40	
	13:00	45	7.8	35:00	155	1.00	
	14:00	50	7.71	36:00	160	0.65	
	15:00	55	7.51	37:00	165	0.42	
30	16:00	60	7.35	38:00	170	0.31	30
	17:00	65	7.12	39:00	175	0.25	
	18:00	70	6.92	40:00	180	0.21	
	19:00	75	6.80	41:00	185	0.20	
	20:00	80	6.52	42:00	190	0.18	
35	21:00	85	6.30	43:00	195	0.15	35
	44:00	200	0.15	61:00	245	0.45	
	45:00	205	0.13	62:00	250	0.41	
	46:00	210	0.11	63:00	255	0.37	
	47:00	215	0.10	64:00	260	0.34	
40	48:00	220	0.10	65:00	265	0.31	40
	49:00	225	0.10	66:00	270	0.28	
	50:00	230	0.10	67:00	275	0.25	
	51:00*	--	0.75	68:00	280	0.23	
	52:00*	--	1.62	69:00	285	0.20	
45	53:00*	--	2.30	70:00	290	0.19	45
	54:00*	--	2.55	71:00	295	0.16	
	55:00*	--	2.85	72:00	300	0.15	
	56:00	--	0.30	73:00	305	0.14	
	57:00	--	0.70	74:00	310	0.13	
50	58:00	--	0.65	75:00	315	0.11	50
	59:00	235	0.55	76:00	320	0.10	
	60:00	240	0.50				

*Aerating Sample

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From Samples 34-43 it is readily apparent that zinc hydrosulfite effectively removes both oxygen and hydrogen sulfide from drilling fluids without adversely affecting the rheology of the drilling fluid.

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EXAMPLE*(Samples 44-54)*

Eleven portions (Samples 44-54) of No. 2 diesel oil were saturated with hydrogen sulfide (H_2S) by bubbling the hydrogen sulfide through the diesel for 1.5 hours. Into each sample a portion of a finely ground scavenger material was placed at a concentration of 10 gm per 350 ml of sample or 10 pounds per 42-gallon barrel (ppb). Each sample was sealed and stirred magnetically for 1.5 hours. The concentration of hydrogen sulfide in each sample was tested by use of a Wickhold combustion apparatus before and after addition of each scavenger material being tested. The hydrogen sulfide scavenger material and percent of hydrogen sulfide removed are tabulated as follows:

TABLE 17

Sample	Scavenger Tested	Percent H_2S Removed
44	CaO	9.2
45	CaCO ₃	32.9
46	Ca(OH) ₂	82.2
47	Zn ₂ (OH) ₂ CO ₃	84.2
48	Zn ₂ (OH) ₂ CO ₃	84.7
49	ZnO	31.8
50	ZnSO ₄	23.8
51	Zn (dust)	25.0
52	Zn.NTS	25.4
53	Fe ₃ O ₃	32.8
54	Na ₂ SO ₃	29.6

Zn.NTS is a zinc-nitrilotriacetic acid complex.

From Samples 44-54 it is readily apparent that basic zinc carbonate ($Zn_2(OH)_2CO_3$) and calcium hydroxide ($Ca(OH)_2$) effectively remove hydrogen sulfide from fluids in which the continuous or external phase is an organic liquid or an oil base mud.

WHAT WE CLAIM IS:-

1. A method of scavenging sulphide from a liquid having a pH of 5 to 12, in which there is used as the scavenging agent a complex formed between at least one zinc compound and an organic chelating agent, the complex having a stability constant of 10 to 16.
2. A method according to claim 1, in which the complex is formed *in situ* in the liquid.
3. A method according to claim 2, in which the liquid is oil-based and the zinc compound is added in the form of a solution or dispersion in oil.
4. A method according to claim 2 or 3, in which the chelating agent is present in excess of the amount needed to chelate all the available zinc.
5. A method according to any of claims 1 to 4, in which the zinc compound contains no anions capable of causing flocculation of any clays in the liquid.
6. A method according to claim 5, in which the zinc compound is a formate, acetate, chloride, bromide, iodide, chlorate, bromate, nitrate, sulphate, sulphonylate, hydrosulphite or silicofluoride salt.
7. A method according to any of claims 1 to 6, in which the chelating agent is a compound having at least one tertiary amine group and at least two carboxyl groups, or a salt thereof.
8. A method according to claim 7, in which the chelating agent is ethylenediamine tetra-acetic acid, β -mercaptoethyliminodiacetic acid, ethylene-bis-N,N'-2(aminomethyl)-pyridine-N,N'-diacetic acid, N-hydroxyethyl ethylene diamine tetra-acetic acid, ethylene diamine-N,N' dipropionic acid-N,N' di-acetic acid, ethylene diamine-N,N' di-acetic acid or ethylene diamine-N,N' di-acetic acid.
9. A method according to claim 7, in which the chelating agent is nitrilotri-acetic acid and/or a salt thereof.
10. A method according to claim 7, in which the chelating agent is a polyfunctional amine or a hydroxy-carboxylic acid.
11. A method according to claim 10, in which the polyfunctional amine is triethylenetetramine, ethylene-bis- α , α' -2(aminomethyl) pyridine, β , β' , β'' tri-aminotriethylamine or α , β -diamino propionic acid.
12. A method according to claim 10, in which the hydroxy-carboxylic acid is dithiotartaric acid.
13. A method according to any of claims 1 to 12, in which the complex contains at least 10% by weight of zinc.

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14. A method according to any of claims 1 to 13, in which the amount of the complex is controlled such that the concentration of sulphide ions in the liquid is maintained below a predetermined amount.

5 15. A method of scavenging sulphide from a liquid having a pH of 5 to 12, in which there is used as the scavenging agent a complex substantially as herein described in any of Samples 2, 5, 9, 11, 13, 14, 19, 21, 22, 23, 26, 28, 30 to 33, or 41 to 54. 5

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